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Relationship between $\delta^{18}O$ values for skeletal apatite from reindeer and foxes and yearly mean $\delta^{18}O$ values of environmental water

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Abstract

The oxygen isotope composition of bone and tooth phosphate of 50 fox specimens and 30 reindeer specimens from various locations with different climatic and environmental conditions was measured. The existing relationship between these values and the mean oxygen isotope composition of local meteoric water has been calculated. In the case of foxes, specimens belonging to two genera (*Vulpes* and *Alopex*) and three different species were measured. The samples fit a straight line whose equation can be used for paleoclimatological studies either in Arctic or in temperate regions. For reindeer (*Rangifer*), a relatively large range of isotopic values was obtained from each location, suggesting imperfect equilibrium conditions with environmental water. The calculated equation can be used for semi-quantitative information on local paleowaters at high latitudes only.

Keywords: Canidae; Rangifer; O-18/O-16; phosphates; numerical models

1. Introduction

Oxygen isotope analyses of mammal bone and tooth phosphate are now widely used for quantitative interpretations of paleoclimatological and paleohydrological conditions according to isotope equations calibrated on modern mammal specimens against the mean oxygen isotope composition of local meteoric water as first proposed by Longinelli [1,2]. Because large mammals have a constant body temperature, the oxygen isotope composition of their skeletal phosphate is directly related to that of their body water. Body water is directly related to ingested water via metabolic fractionation and, at least for animals that do not migrate, to the mean oxygen isotope composition of local meteoric water ($\delta^{18}O_w$). The mean $\delta^{18}O$ value of meteoric water is correlated [3] to the mean annual air temperature. It follows that the oxygen isotope composition of fossil skeletal material may provide a quantitative record of paleoclimatic conditions during the life of the fossil mammals studied (e.g. [4,5]).

Despite taphonomic and diagenetic changes which skeletal remains normally undergo and which may affect the pristine oxygen isotopic composition, quantitative information on paleo-

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climatic conditions may be obtained at least in the case of relatively recent fossils of Holocene and Pleistocene age. In the case of older fossils tooth enamel is generally preferred being more resistant to diagenetic changes [4–9]. Nine isotope equations calibrated on humans, pigs, deer, mice, cattle, sheep, elephants, horses, roebuck deer and goats are available up to now for terrestrial mammals.

To extend the application of this method as far as possible to the study of different climatic conditions and environments in the past, it is of importance to calibrate as many isotope equations as possible. Unfortunately, specimens of modern mammals living under 100% natural conditions are very difficult to find. Almost all recent mammals feed, at least partially, on man-made food, particularly during winter or when they are restricted to stay within the limits of national and regional parks. Man-made food can alter the environmental and biological conditions and, as a consequence, the relationship normally existing between the $\delta^{18}O$ values of body water and the mean $\delta^{18}O$ values of environmental water is modified. Previous measurements (e.g. [10]) showed measurable deviations from the expected values of body water and the bone oxygen isotope composition in the case of animals that were partially fed with man-made food.

The $\delta^{18}O$ values obtained from fox and reindeer bone and tooth phosphate are reported here. The samples come from different areas with different climatic and/or environmental conditions. Fossil fox bones and teeth are frequently found in Holocene deposits and the availability of a calibrated fox isotope equation is of importance for paleoclimatic studies. Reindeer teeth and bones are the most common fossils found in Northern Russia and Siberia, along with mammoth skeletal remains. The availability of a reindeer isotope equation would greatly help paleoclimatological studies of the extreme conditions dominating the vast northern areas during both Pleistocene and Holocene.

2. Materials and methods

The tooth enamel samples were collected from the collar to the apex to represent the whole period of tooth accretion and to reduce the intratooth variation related to seasonal changes in climate. The samples were prepared according to the protocol outlined by Crowson and Showers [11], slightly modified by Lécuyer et al. [12]. The procedure can be summarized as follows: a 30% H_2O_2 solution is added to 40–50 mg of powdered clean bone or enamel and left at 100°C for 3–7 days to oxidize the organic matter. The sample is then rinsed in double distilled water and dried at 50°C. Two ml of 2 M HF solution are then added and each phosphate sample is dissolved at room temperature for 24 h. The solution is centrifuged and the solid residue eliminated. This solution is neutralized with about 2 ml of 2 M KOH and 2 ml of Amberlite (IRA 400 OH) are added to absorb the PO_4^{3-} ions while the system is gently shaken on a rotating device for 24 h. The supernatant is then eliminated and the Amberlite rinsed with distilled H_2O; 28 ml of 0.5 M NH_4NO_3 are added to the solution to release the PO_4^{3-} ions and the system is again gently shaken for 4 h. At this point the resin is eliminated, 15 ml of 0.2 M Ag_3NO_3 are added to the solution, and the solution is left for about 7 h at 70°C to precipitate the Ag_3PO_4 which is filtered and dried at 60°C. The Ag_3PO_4 crystals are reacted with BrF_5 at about 600°C for 15 h. The oxygen obtained from the reaction is converted to CO_2 by cycling over hot graphite in the presence of a Pt catalyst and the isotope composition of CO_2 measured on a Finnigan Delta S mass spectrometer. Stable isotope ratios are reported versus V-SMOW in the standard δ notation (in permil). The standard deviation of our measurements was better than $\pm 0.15‰$ (1σ).

3. Results and discussion

3.1. Foxes

The mean $\delta^{18}O$ values obtained from fox samples are reported in Table 1 along with the mean annual $\delta^{18}O$ values of local meteoric water. The samples are from teeth and bones of modern specimens belonging to two different genera:

Table 1
Oxygen isotope composition of bone and tooth phosphate ($\delta^{18}O_p$) of recent foxes from different locations and the oxygen isotope composition of local meteoric water ($\delta^{18}O_w$)

Sample	Species	Elevation	Material	$\delta^{18}O_p$	$\delta^{18}O_w$
Italy-Circeo N.P./1	*Vulpes vulpes*	about sea level	jaw	18.0	−5.8
Italy-Circeo N.P./2	*Vulpes vulpes*	about sea level	jaw	18.1	−5.8
Italy-Circeo N.P./3	*Vulpes vulpes*	about sea level	jaw	17.9	−5.8
Italy-Circeo N.P./4	*Vulpes vulpes*	about sea level	jaw	18.0	−5.8
Italy-Circeo N.P./5	*Vulpes vulpes*	about sea level	jaw	18.2	−5.8
Italy-Circeo N.P./6	*Vulpes vulpes*	about sea level	tooth/m^3	18.0	−5.8
Italy-Circeo N.P./7	*Vulpes vulpes*	about sea level	tooth/m^2	17.9	−5.8
Italy-Circeo N.P./8	*Vulpes vulpes*	about sea level	tooth/m^1	18.0	−5.8
Italy-Circeo N.P./9	*Vulpes vulpes*	about sea level	tooth/p^4	18.2	−5.8
Italy-Circeo N.P./10	*Vulpes vulpes*	about sea level	tooth/p^3	18.1	−5.8
Italy-Circeo N.P./11	*Vulpes vulpes*	about sea level	tooth/p^2	18.2	−5.8
Italy-Circeo N.P./12	*Vulpes vulpes*	about sea level	tooth/p^1	17.8	−5.8
Italy-Circeo N.P./13	*Vulpes vulpes*	about sea level	tooth/c	18.1	−5.8
Italy-Circeo N.P./14	*Vulpes vulpes*	about sea level	tooth/m^1	18.0	−5.8
Italy-Circeo N.P./15	*Vulpes vulpes*	about sea level	tooth/m^2	18.0	−5.8
Italy-Circeo N.P./16	*Vulpes vulpes*	about sea level	tooth/p^4	18.1	−5.8
Italy-Circeo N.P./17	*Vulpes vulpes*	about sea level	tooth/p^3	18.1	−5.8
Italy-Circeo N.P./18	*Vulpes vulpes*	about sea level	tooth/p^2	17.9	−5.8
Italy-Circeo N.P./19	*Vulpes vulpes*	about sea level	tooth/p^1	18.1	−5.8
Italy-Circeo N.P./20	*Vulpes vulpes*	about sea level	tooth/c	17.9	−5.8
Italy-Circeo N.P./21	*Vulpes vulpes*	about sea level	tooth/i^3	18.0	−5.8
Italy-Circeo N.P./22	*Vulpes vulpes*	about sea level	tooth/i^2	18.0	−5.8
Italy-Circeo N.P./23	*Vulpes vulpes*	about sea level	tooth/i^1	17.9	−5.8
Wales/372	*Vulpes vulpes*	up to 830 m	pelvis	15.7	−7.2
Wales/388	*Vulpes vulpes*	up to 830 m	vertebra	15.6	−7.2
Wales/404	*Vulpes vulpes*	up to 830 m	jaw	15.3	−7.2
Wales/367	*Vulpes vulpes*	up to 830 m	rib	15.2	−7.2
Wales/75	*Vulpes vulpes*	up to 830 m	tooth/p^4	15.0	−7.2
N Sweden (Lappmark)/1	*Alopex lagopus*	about 1000 m	bone	10.3	−11.0
N Sweden (Lappmark)/2	*Alopex lagopus*	about 1000 m	bone	10.8	−11.0
N Sweden (Lappmark)/3	*Alopex lagopus*	about 1000 m	bone	10.8	−11.0
N Sweden (Lappmark)/4	*Alopex lagopus*	about 1000 m	bone	10.9	−11.0
NW Iceland (Stranda)/6	*Alopex lagopus*	about sea level	bone	14.9	−8.2
NW Iceland (Stranda)/7	*Alopex lagopus*	about sea level	bone	15.1	−8.2
NW Iceland (Stranda)/8	*Alopex lagopus*	about sea level	bone	14.6	−8.2
NW Iceland (Stranda)/9	*Alopex lagopus*	about sea level	bone	15.0	−8.2
NW Iceland (Stranda)/10	*Alopex lagopus*	about sea level	bone	14.6	−8.2
NW Iceland (Stranda)/11	*Alopex lagopus*	about sea level	bone	14.6	−8.2
Almeria/1	*Vulpes vulpes*	400–500 m	tooth/m^1	18.5	−5.5
Almeria/12	*Vulpes vulpes*	400–500 m	tooth/m^1	18.3	−5.5
Cordoba/2	*Vulpes vulpes*	100–200 m	tooth/m^1	18.1	−5.3
Huelva/3	*Vulpes vulpes*	about sea level	tooth/m^1	18.7	−4.7
Pontevedra/5	*Vulpes vulpes*	0–200 m	tooth/m^1	18.3	−5.2
Oviedo/8	*Vulpes vulpes*	∼200 m	tooth/m^1	18.4	−5.3
Orgiva (Granada)/11	*Vulpes vulpes*	700–800 m	tooth/m^1	17.1	−6.4
Orgiva (Granada)/13	*Vulpes vulpes*	700–800 m	tooth/m^1	16.8	−6.4
Santander/15	*Vulpes vulpes*	200–300 m	tooth/m^1	18.5	−5.3
Madrid/16	*Vulpes vulpes*	600–700 m	tooth/m^1	16.6	−7.0
La Coruña/18	*Vulpes vulpes*	200–300 m	tooth/m^1	18.1	−5.3
Spanish Sahara/4	*Canis aureus*		tooth/m^1	21.8	−3.0
Spanish Sahara/6	*Canis aureus*		tooth/m^1	22.0	−3.0
Morocco/17	*Vulpes zerda*		tooth/m^1	20.1	−4.0

Vulpes (*V. vulpes* and *V. zerda*) and *Alopex* (*A. lagopus*). The specimens come from different areas ranging from Sweden to Morocco, covering the largest possible range of isotope compositions of local meteoric water. The mean $\delta^{18}O$ values of local precipitation was measured directly in the studied areas or extrapolated from the data published by the IAEA in Vienna (IAEA reports on environmental isotope data). For Circeo National Park (Central Italy) five jaws belonging to specimens of *V. vulpes* (red fox) were analyzed along with two sets of teeth in order to investigate bone–tooth and inter-tooth compositional variability (Table 1). One set (samples 6–13) has been taken from the right side of the jaw reported in Table 1 as sample 3, where the incisors were missing, the other set (samples 14–23) from the left side of the jaw reported as sample 4. Compositional homogeneity among different teeth is apparent in the two individual jaws, between the two sets of samples and also between tooth and bone samples (mean oxygen isotope composition of phosphate ($\delta^{18}O_p$) value +18.0 ± 0.11 vs. V-SMOW). This homogeneity of isotope compositions could probably be ascribed to the fact that permanent teeth grow more or less in the same period and/or that the variability of the oxygen isotope composition of the total oxygen taken up is relatively small throughout the year. It is apparent that the enamel oxygen isotope composition is not affected by the nursing effect which tends to enrich in ^{18}O the tooth [13,14]. We can conclude that for foxes all the permanent teeth and bones can be used to calibrate the relationship between $\delta^{18}O_p$ and $\delta^{18}O_w$.

Table 2
Oxygen isotope composition of bone and tooth phosphate ($\delta^{18}O_p$) of recent reindeer from different locations and the oxygen isotope composition of local meteoric water ($\delta^{18}O_w$)

Sample	Material	$\delta^{18}O_p$	$\delta^{18}O_w$
Svalbard Islands	bone	12.9	−10.0
Svalbard Islands	bone	12.4	−10.0
Svalbard Islands	bone	11.9	−10.0
Svalbard Islands	tooth	14.5	−10.0
Svalbard Islands	tooth	12.7	−10.0
Svalbard Islands	tooth	11.6	−10.0
Lapponia-Rovaniemi	bone	13.0	−12.0
Lapponia-Rovaniemi	bone	12.1	−12.0
Lapponia-Rovaniemi	bone	11.8	−12.0
Lapponia-Rovaniemi	bone	11.6	−12.0
Lapponia-Rovaniemi	bone	11.3	−12.0
Lapponia-Rovaniemi	bone	11.1	−12.0
Lapponia-Rovaniemi	bone	10.9	−12.0
Lapponia-Rovaniemi	bone	10.8	−12.0
Lapponia-Rovaniemi	bone	10.5	−12.0
Lapponia-Rovaniemi	bone	9.9	−12.0
Lapponia-Rovaniemi	bone	10.8	−12.0
Norwegian Lapland	tooth	12.1	−12.5
Norwegian Lapland	tooth	11.4	−12.5
Novaya Zemlya	bone	8.9	−16.0
Novaya Zemlya	tooth	10.8	−16.0
Novaya Zemlya	tooth	10.8	−16.0
Novaya Zemlya	tooth	10.6	−16.0
Novaya Zemlya	tooth	8.3	−16.0
Novaya Zemlya	tooth	7.9	−16.0
Belyj Island	tooth	10.0	−18.0
Belyj Island	tooth	7.9	−18.0
Siberyhova Island	tooth	8.6	−18.0
Siberyhova Island	tooth	7.0	−18.0
Nadym river	bone	6.9	−18.5
Nadym river	tooth	9.0	−18.5
Nadym river	tooth	6.3	−18.5
Nadym river	tooth	5.4	−18.5
Nadym river	tooth	5.4	−18.5
Faddeevsky Island	bone	6.3	−24.0
Bel'kovsky Island	bone	7.6	−24.0

The $\delta^{18}O_p$ values of all the tooth samples analyzed from Spain range from +16.6 to +18.7‰. They belong to specimens of *V. vulpes* and refer systematically to the first molar (m1). They were collected at different locations from sea level to about 700/800 m a.s.l. The sample from Morocco belongs to *V. zerda* and has the most positive $\delta^{18}O_p$ value measured (+20.1‰). The four bone and one tooth (p^4) samples from Wales belong to *V. vulpes*. Their $\delta^{18}O_p$ values range from +15.0‰ to +15.7‰, the width of this range being justified by the different elevations of the collecting sites. Samples from Sweden and Iceland belong to the species *A. lagopus* (common name: Arctic fox). These specimens come from inland and coastal sites respectively and show rather narrow ranges of $\delta^{18}O_p$ values: from +10.3 to +10.9 for the former and from +14.6 to +15.1 for the latter.

The data obtained are reported graphically in Fig. 1 and a least squares best fit yields the following equation:

$$\delta^{18}O_p = 1.34\,\delta^{18}O_w + 25.49\ (R^2 = 0.98) \quad (1)$$

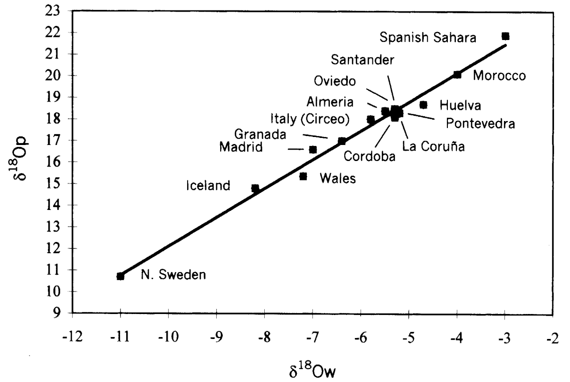

Fig. 1. Relationship between the mean annual oxygen isotope composition of local meteoric water ($\delta^{18}O_w$) and the mean oxygen isotope composition of bone and tooth phosphate ($\delta^{18}O_p$) of recent foxes.

Two isotopic values from specimens of *Canis aureus* from the Spanish Sahara are also reported even though these values were not used to calculate Eq. 1. Their compositions fit well the calibration line obtained for *Vulpes* and *Alopex*. This could suggest that different genera belonging to the family Canidae show a similar phosphate–water fractionation factor. Obviously, two specimens are insufficient to prove this assumption and further measurements are needed for this purpose.

3.2. Reindeer

The mean $\delta^{18}O$ values obtained from samples of *Rangifer tarandus* (reindeer) are reported in Table 2 along with the mean annual $\delta^{18}O$ values of local meteoric water. These values were measured directly or extrapolated from the data published by the IAEA in Vienna (reports on environmental isotope data). We were able to measure a number of bone and tooth samples of modern reindeer from climatically different areas in Northern Europe and Northern Siberia. With the exception of specimens from Norwegian Lapland all other groups have a wide range of isotopic values, from 1.3 to 3.6‰. This huge variance of the oxygen isotope values at each sampling site may be ascribed to different reasons such as:

1. the use of teeth. Normally, the range of variation for $\delta^{18}O_p$ values of teeth is larger than that of bones. This can be related to the fact that tooth phosphate is not renewed during the lifetime of an individual and, consequently, the isotope composition refers to a very short period of the specimen's life [15,16]. However, it must be pointed out that the variability of $\delta^{18}O_p$ values in the Rovaniemi group (only one tooth was measured) is 3.1‰, comparable to that measured for teeth;
2. values of the relative humidity. All the reindeer samples come from high latitude locations, at or even above the Arctic Circle where the relative humidity is low, particularly during winter. Measuring bones of white-tailed deer from N. America and rabbits from Spain, Luz et al. [17] and Delgado Huertas et al. [18], respectively, showed that samples from locations with low humidities are ^{18}O enriched when compared to samples coming from humid areas, even in the case of similar $\delta^{18}O$ values of local precipitations. This is because white-tailed deer and rabbits obtain most of their water from leaves and/or grass whose $\delta^{18}O$ values are partly controlled by relative humidity, via evapotranspiration processes. Moreover, the output of water vapor during respiration and the fractionation between this vapor and body water may also change as a function of humidity;
3. specimens from the same area may belong to

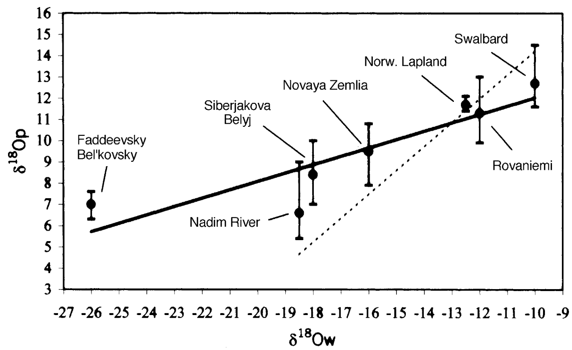

Fig. 2. Relationship between the mean annual oxygen isotope composition of local meteoric water ($\delta^{18}O_w$) and the mean oxygen isotope composition of bone and tooth phosphate ($\delta^{18}O_p$) of recent reindeer. The range of the $\delta^{18}O_p$ values is also reported. The dashed line refers to the equation for deer [10].

different herds with different water input related to different oxygen isotopic composition of drinking water (snow in winter) and/or to differences in diet;

4. the effect of man-made food. In the case of the Northern Norway and Northern Finland sites reindeer herds may be partly fed by humans;
5. in the case of wild herds, reindeer may move through relatively large areas.

We should also point out that there are minor uncertainties in the assignment of the $\delta^{18}O$ values of local meteoric water in the case of the Novaya Zemlya, Nadym river, and Belyj, Siberyhova and Faddeevsky islands sites, the isotope data available for Siberia and Arctic areas, as measurements are rare and not always statistically reliable. Under these conditions the use of the reindeer equation for *quantitative* paleoclimatological reconstruction is limited.

The least squares best fit calculated from the results obtained (Fig. 2) yields the following equation:

$$\delta^{18}O_p = 0.39\ \delta^{18}O_w + 15.96\ (R^2 = 0.79) \tag{2}$$

So far the deer equation (*Cervus elaphus*) has been used to calculate the $\delta^{18}O$ values of paleowater for fossil reindeer samples on the basis that these two genera belong to the same family. The line of the deer equation is also reported in Fig. 2 and it can be seen that the slopes of the two equations are rather different from one another. However, if the two dates from the Faddeevsky and Bel'kovsky islands are left out the slope of the best fit line would be considerably closer to that of the deer equation.

4. Summary

About 80 bone and tooth samples of fox and reindeer have been measured for their $\delta^{18}O_p$ values. The data obtained allow the calculation of equations relating the $\delta^{18}O_p$ values to those of the mean annual local meteoric water. The equation for foxes can be used for quantitative paleoclimatological studies of environmentally different areas, from tropical to polar conditions. It has been shown that both fossil bone and tooth samples are suitable for this purpose. The reindeer equation, however, is recommended only for semi-quantitative reconstructions of paleoclimates at high latitudes because of the relatively large range of $\delta^{18}O_p$ values obtained from each sampling site and because of some uncertainty regarding the precise value of local mean $\delta^{18}O_w$ at some of the sampling sites. The reindeer equation is somewhat different from that of deer, this difference being quite difficult to explain lacking quantitative information on the metabolic processes of these two mammals.

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